Review

# Solid state electrochemical DeNO$_x$—An overview

K. Kammer Hansen *

Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark

ABSTRACT

The literature on direct electrochemical reduction of NO$_x$ in a solid state cell has been reviewed. It is shown that the reduction of nitric oxide either occurs on the electrode or on the electrolyte if F-centers are formed. It is also shown that some oxide based electrodes has a high apparent selectivity towards the reduction of nitric oxide in a net oxidizing atmosphere. The activity and apparent selectivity of oxide based electrodes is strongly dependent on the composition of the oxide. The selectivity of noble metal based electrodes is generally very low. However, coating of noble metal based electrodes can give current efficiencies of up to 20% even in the presence of large amounts of oxygen.

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## Contents

## 1. Introduction

The exhaust gas emitted from the combustion process of fossil fuels contains significant amounts of NO$_x$ [1]. The emission of NO$_x$ is highly unwanted, as NO$_x$ lead to the formation of smog and acid rain [2,3]. Several processes are known that can reduce the NO$_x$ from diesel exhausts. The best known commercial solution is the selective catalytic reduction (SCR) of NO$_x$ using urea as a reducing agent [4]. The main problems with this method is that the reducing agent has to be stored on-board the vehicle, and that possible slip of the reducing agent is a serious threat. The formation of nitrous oxide (a powerful greenhouse gas) is another problem, that hasn't been solved [5]. Electrochemical reduction of NO$_x$ in an all solid state electrochemical reactor is a potential attractive technique [6]. In electrochemical reduction of NO$_x$ current is used instead of a reducing agent. The concept is shown in Fig. 1. In the figure it is seen that nitric oxide is reduced at the cathode to nitrogen and oxide anions. The oxide anions are transported through the electrolyte

to the anode where oxygen is formed. Some reviews on solid state electrochemical DeNO$_x$ have already been published most of them several years ago [6–10]. This is an up to date and more in depth review.

## 2. General considerations

The constituents and the temperature of the exhaust of different types of engines are shown in Table 1. It is seen that the exhaust of a typical diesel engine contains 200–1000 ppm of NO$_x$, besides other pollutants. In this context the high amount of oxygen present in the exhaust gas should be noted.

Solid state electrochemical DeNO$_x$ is build on the SOFC technology. The operation temperature of the SOFC is typically around 750 °C. The temperature of the exhaust gas of a diesel engine is much lower, 300 °C or even lower. Questions on the activity arise from this. The activity is therefore one problem that has to be tackled to make solid state electrochemical DeNO$_x$ useful for practical applications.

The high amount of oxygen is another issue to be addressed. Oxygen can be reduced along with nitric oxide at the cathode. If oxygen is reduced before nitric oxide this will lead to a very low
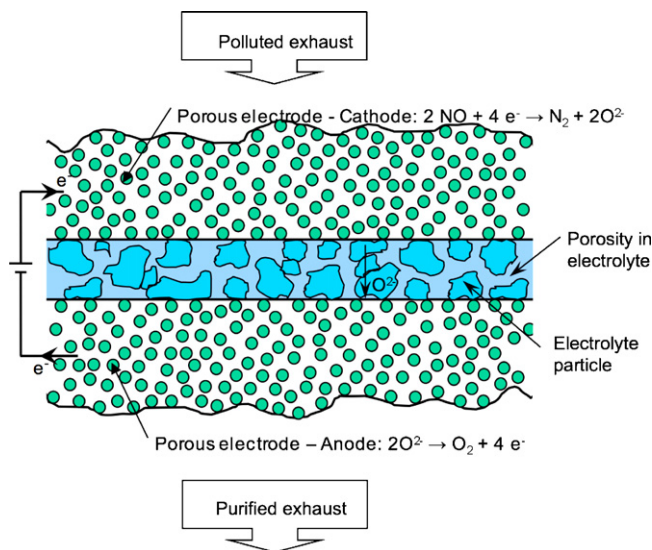
* Corresponding author. Tel.: +45 4677 5835; fax: +45 4677 5858.
E-mail address: kkha@risoe.dtu.dk.

**Table 1**
The constituents in different exhaust gasses.

| | CO (%) | HC (ppm) | NO$_x$ (ppm) | Particulate (g kWh$^{-1}$) | O$_2$ (%) | Temp. (°C) |
|---|---|---|---|---|---|---|
| Otto | 0.3–1 | 1000–5000 | 50–2500 | – | 0.1–0.5 | 150–1000 |
| Otto lean-burn | 0.05–0.5 | 1000–5000 | 100–1000 | – | 0.5–5 | 100–900 |
| Diesel | 0.01–0.2 | 100–2000 | 200–1000 | 0.15–0.5 | 3–15 | 80–700 |



**Fig. 1.** A sketch of an electrochemical reactor for removal of nitric oxide. The reactor is seen to consist of an electrolyte and a pair of electrodes. The reduction of nitric oxide occurs at the cathode.

current efficiency. The selectivity is therefore another issue that has to be solved before solid state electrochemical DeNO$_x$ can be made a success. Almost all the literature concerning solid state electrochemical DeNO$_x$ has focused on the selectivity.
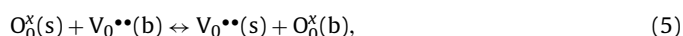
In Fig. 2 theoretical calculations on the extent of reaction as a function of potential at 400 °C is shown. It is seen that the reduction of nitric oxide to nitrogen is initiated at very high potentials, approximately 0.5 V vs. air, compared to the potential where the reduction of oxygen is initiated. This is also illustrated in Fig. 3. It is seen that the anti-bonding orbitales of nitric oxide is placed at a lower energy level than the anti-bonding orbitales of oxygen that
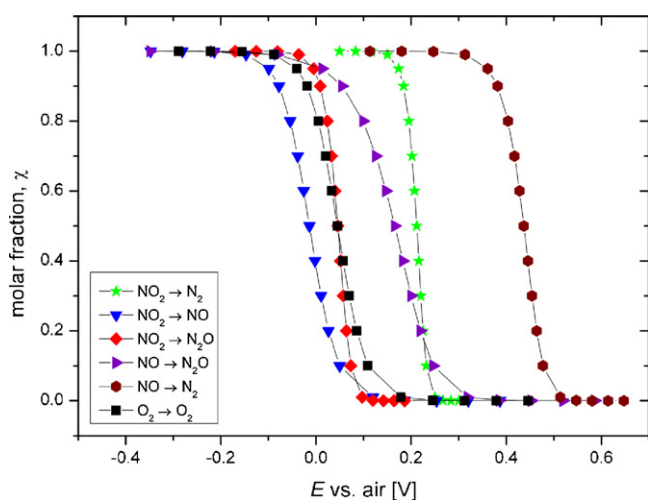


**Fig. 2.** Extent of reaction as a function of potential for different gaseous reactions. The black squares are representing the oxygen exchange reaction, which is pumping of oxygen of from one side of the cell to the other side of the cell. The higher the potential is the lower is the relative stability of the given molecule.
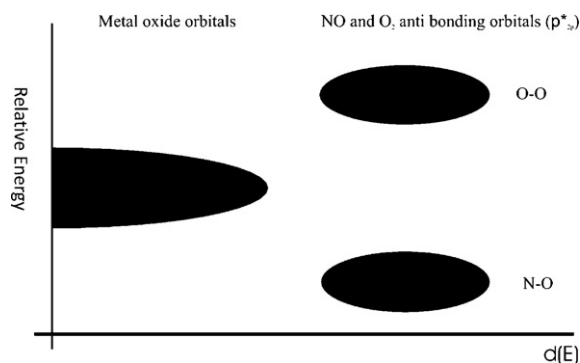


**Fig. 3.** Schematic picture of the energy level of the valence electrons of a metal oxide and the anti-bonding orbitales of nitric oxide and oxygen. The $d(E)$ on the x-axis denotes the density of states.

is nitric oxide is less stable than oxygen. It is also seen from Fig. 2 that the reduction of nitric oxide to nitrous oxide is initiated at a lower potential than the reduction of nitric oxide to nitrogen. Based on thermodynamic considerations alone it is therefore possible to reduce nitric oxide selectively to nitrogen by a careful control of the applied potential. However, oxidation of nitric oxide to nitrogen dioxide must also be taken into account. As it can be seen from Fig. 2 nitric oxide is oxidized to nitrogen dioxide at potentials above approximately 0 V vs. air. This is the same as saying that nitric oxide is thermodynamic unstable at 400 °C, as nitric oxide can be reduced and oxidized in the same potential window.

## 3. Literature survey

*Early work.* The idea of reducing NO$_x$ electrochemical in an all solid state cell was first suggested by Pancharatnam et al. [11] in 1975. Using a Scandia Stabilized Zirconia (SSZ) electrolyte and either porous platinum or porous gold electrodes they showed that nitric oxide could be reduced at the cathode to N$_2$ and oxide anions in the temperature range of 600–800 °C. By applying very high overpotentials (−2.2 V vs. air) it was furthermore shown that the rate of the reduction of nitric oxide exceeded the Faradaic value by a thousand fold. The results indicated that the reduction of nitric oxide occurred on the zirconia surface and not on the electrodes. When high cathodic potentials are applied to a zirconia based cell, the zirconia is reduced (blackening). The blackening of zirconia is due to the formation of F-centers. The mechanism below was suggested by the authors

$$V_0^{\bullet\bullet}(s) \leftrightarrow V_0^x(s) + 2h_{electrode}^{\bullet} \tag{1}$$

$$NO + V_0^{\bullet\bullet}(s) \rightarrow N\text{–}O_0^x(s) \tag{2}$$

$$NO + N\text{–}O_0^x(s) \rightarrow N_2O + O_0^x(s) \tag{3}$$

$$N_2O + V_0^x(s) \rightarrow N_2 + O_0^x(s) \tag{4}$$

$$O_0^x(s) + V_0^{\bullet\bullet}(b) \leftrightarrow V_0^{\bullet\bullet}(s) + O_0^x(b), \tag{5}$$

where $V_0^x$ is a F-center, (s) denotes the surface of electrolyte and (b) the bulk of the electrolyte. In a later work by Gür and Huggins [12] this mechanism was confirmed using platinum and gold point electrodes.

**Table 2**
Noble metal based cathodes.

| Cathode, electrolyte | Temperature range | Concentration of NO | Concentration of $O_2$ | Selectivity | Current efficiency | Reference |
|---|---|---|---|---|---|---|
| Pt, SSZ | 600–800 °C | 1–100% | – | – | – | [11,12] |
| Au, SSZ | 600–800 °C | 1–100% | – | – | – | [11,12] |
| Pt, YSZ | 600–800 °C | 1000 ppm | – | – | – | [13] |
| Pd, YSZ/CSO | 550–900 °C | 1000 ppm | 2–10% | – | 1.5% | [14,15,17] |
| Pt, YSZ | 500–600 °C | 0–610 ppm | 3.1–9.8% | 0.6 | – | [18] |
| Ir, YSZ | 500–600 °C | 230–610 ppm | 0.1–9.8% | 1.6 | – | [19] |
| Pd, YSZ | 450 °C | 1500 ppm | 3% | – | 2% | [20,21] |
| Pt, YSZ | 800 °C | 1000 ppm | – | – | – | [22] |
| Au, CGO | 400–600 °C | 1% | – | – | – | [23] |
| Pt, CGO | 400–600 °C | 1% | – | – | – | [23] |

*Later work.* Later research work can be divided into three areas; noble metal electrodes, pure oxide based electrodes and coating of metal based electrodes.

*Noble metals* (*this paragraph is taken from* [9] *in slightly edited form*): In a work by Gessner et al. [13] in 1988 the activity of gas mixtures containing nitric oxide, nitrogen dioxide and oxygen on platinum electrodes was investigated at 600–800 °C using a YSZ electrolyte. The authors concluded that oxygen exchange is not always the dominant charge transfer reaction. That is, the reduction of nitrogen dioxide to nitric oxide and the oxidation of nitric oxide to nitrogen dioxide were found to be the dominant charge transfer reactions (Table 2).

In the first of a series of publications Hibino [14] investigated the simultaneous reduction of nitric oxide and oxidation of methane. A mixture of nitric oxide (1000 ppm), oxygen (2–10%) and methane (1000 ppm) was added to a Pd|YSZ|Pd cell at 700 °C. It was shown that nitric oxide was reduced to nitrogen at the cathode and that methane was oxidised to carbon dioxide at the anode. In a later work by the same author it was proposed that nitric oxide was reduced to nitrogen at the cathode (and not on the zirconia surface) [14]. That is

$$2NO \rightarrow N_2 + 2O^{2-} + 4h^\bullet \tag{6}$$

The reduction according to (6) took place in competition with the reduction of oxygen. In a later work experiments were conducted on the same type of cell in the temperature interval of 550–900 °C [15]. The current efficiency for the reduction of nitric oxide was reported to be as low as 1.5% independent of the operating temperature of the cell. Later Hibino et al. [16] used solid electrolyte potentiometry (SEP) to investigate the mechanism of the reduction of nitric oxide on palladium electrodes using a $Ce_{0.8}Sm_{0.2}O_{1.9}$ electrolyte. It was found that the poorer the oxygen pumping properties of the cell was the higher was the current efficiency. This means that if the three-phase boundary is very small then the rate of the dissociation of oxygen is very low (as it happens primarily at the three phase boundary). The current efficiency for the reduction of nitric oxide will then be increased.

In 1996 Hibino et al. [17] investigated the effect of water and oxygen on the rate of the reduction of nitric oxide in a ceria electrolyte based cell with palladium electrodes. It was shown that both oxygen and water had a negative influence on the rate of the reduction of nitric oxide. It was shown than the rate of the decomposition of nitric oxide was dependent on the oxygen-pumping rate. The more oxygen removed from the cathode the higher was the nitric oxide decomposition rate.

A detailed kinetics study was performed by Walsh et al. on platinum [18] and iridium [19] electrodes using a YSZ electrolyte. Whereas the platinum electrodes revealed no selectivity the iridium electrode showed a limited selectivity towards the reduction of nitric oxide. Cyclic voltammetry revealed that the platinum electrode is more active for the reduction of nitric oxide when platinum is in its metallic state and not on the form of platinum dioxide.

The same is true for the iridium electrode, where it was shown that iridium metal selectively reduces nitric oxide in the presence of oxygen. However, the rate of reduction of nitric oxide was only around 1.6 times higher than the oxygen reduction rate. The selectivity was found to increase with decreasing temperature. The following mechanism was suggested for iridium electrodes by the authors:

$$NO(g) + (s) \rightarrow \frac{1}{2}N_2(g) + O_{ad} \tag{7}$$

$$O_2(g) + 2(s) \leftrightarrow 2O_{ad} \tag{8}$$

$$O_{ad} + S_{e-e} \leftrightarrow O_{e-e} + (s) \tag{9}$$

$$O_{e-e} + V_0^{\bullet\bullet} \leftrightarrow O_o^x + S_{e-e} + 2h^\bullet \tag{10}$$

where $S_{e-e}$ denotes a site at the electrolyte–electrode contact area.

In a more recent study Hibino et al. [20,21] investigated the effect of applying alternating current to YSZ based cells with porous gold, palladium, platinum or rhodium electrodes, instead of using direct current. The current efficiency was shown to be highest when a palladium electrode was used in combination with an applied alternating voltage higher than 3 V. When potentials lower than 3 V were applied to the cell direct current was the most efficient. The cells showed the highest current efficiency at the lowest temperature. However, in a gas mixture containing 1500 ppm nitric oxide and 3% oxygen the current efficiency was only around 2% at a temperature of 450 °C.

In 2000 Kaneko et al. [22] showed that nitric oxide injected in pulses could be reduced at a temperature of 800 °C using a Pt electrode and an YSZ electrolyte at relatively high potentials (−500 mV vs. air). However, no oxygen was introduced into the reaction chamber.

Kammer Hansen [23] studied the reduction of oxygen and nitric oxide on point electrodes of either gold or platinum in the temperature range of 400–600 °C. It was shown that gold was almost inactivity towards the reduction of nitric oxide, but had some activity towards the reduction of oxygen. The activity of platinum towards the reduction of nitric oxide and oxygen was almost the same. The results indicate that the electrode materials have to be catalytic active in order to be able to reduce nitric oxide electrochemically.

*Pure oxide based electrodes.* The first example of the use of oxide based electrodes was presented in the literature in 1990 [24]. Using a metal oxide based cathode (no information given on the exact composition) a reduction of nitric oxide of 91% was achieved with an oxygen content of up to 8% in the temperature range of 650–1050 °C. The magnitude of the current efficiency was not given in the reference (Table 3).

Later Reinhardt et al. [25] studied the effect of nitric oxide and nitrogen dioxide on the rate of the reduction of oxygen on $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ based electrodes in the temperature range of 500–900 °C. The authors claimed that the rate of the reduction of oxygen increased when nitric oxide was added to the test gas.

**Table 3**
Pure oxide based cathodes.

| Cathode, electrolyte | Temperature range | Concentration of NO | Concentration of $O_2$ | Selectivity | Current efficiency | Reference |
|---|---|---|---|---|---|---|
| Metal oxide, YSZ | 650–1050 °C | 1% | 8% | – | – | [25] |
| $La_{0.8}Sr_{0.2}MnO_3$, YSZ | 500–900 °C | 0–3270 ppm | 1–20% | – | – | [26] |
| NiO, YSZ | 400–600 °C | 1% | – | – | – | [23] |
| CuO, CGO | 300–500 °C | 2% | – | – | – | [27] |
| $CuCr_2O_4$, CGO | 300–500 °C | 1% | – | – | – | [28] |
| $CoFe_2O_4$, YSZ | 400–600 °C | 1% | – | – | – | [29] |
| $NiFe_2O_4$, YSZ | 400–600 °C | 1% | – | – | – | [29] |
| $CuFe_2O_4$, YSZ | 400–600 °C | 1% | – | – | – | [29] |
| $Co_3O_4$, YSZ | 400–600 °C | 1% | – | – | – | [29] |
| $Ni_{1-x}Mg_xFe_2O_4$, YSZ | 400–600 °C | 1% | – | – | – | [30] |
| $NiFe_{2-x}Cr_xO_4$, YSZ | 300–600 °C | 1% | – | – | – | [31] |
| $MgFe_{2-x}Mn_xO_4$, YSZ | 300–600 °C | 1% | – | – | – | [32] |
| $La_{0.85}Sr_{0.15}CoO_3$, CGO | 300–500 °C | 2% | – | – | – | [33] |
| $La_{1-x}Sr_xMnO_3$, CGO | 300–500 °C | 2% | – | – | – | [28,33,34] |
| $La_{0.6}Sr_{0.4}Mn_{1-x}Fe_xO_3$, CGO | 300–500 °C | 2% | – | – | – | [34] |
| LSCF + CGO, CGO | 600 °C | 1000 ppm | 2% | – | 2.5% | [40] |
| LSM + YSZ, SSZ | 600 °C | 1000 ppm | 2% | – | – | [41] |
| LSCF + Pt + CGO, CGO | 600 °C | 1000 ppm | 2% | – | 4.0% | [42] |
| $La_{2-x}Sr_xCuO_4$, YSZ | 400–600 °C | 1% | – | – | – | [39] |
| $La_{2-x}Sr_xNiO_4$, YSZ | 400–600 °C | 1% | – | – | – | [40] |

However, as no gas analysis was undertaken in the study, it is not possible to rule out that the increased current density, when adding nitric oxide to the test gas, was due to the reduction of nitric oxide itself.

Wachsman et al. [26] showed that a $La_{0.8}Sr_{0.2}Co_{0.9}Ru_{0.1}O_{3-\delta}$ cathode was more effective in reducing nitric oxide than a Pt-based cathode under net oxidising conditions. This was attributed to good electro-catalytic properties of the perovskite based cathode compared to the Pt-based cathode.

In a series of papers Kammer Hansen et al. [23,27–37] studied the reduction of nitric oxide and oxygen on cone-shaped electrodes. The simple oxides NiO and CuO were investigated in two papers [23,27]. It was shown that NiO has almost no activity towards the reduction of nitric oxide, whereas CuO is highly active towards the electrochemical reduction of nitric oxide. This is the same trend as observed for the direct catalytic decomposition of nitric oxide on these two oxides, where it is known that CuO is more active than NiO [38,39]. This indicates that the bond breaking of nitric oxide is rate limiting for the electrochemical reduction of nitric oxide on these two compounds. It was also shown that when NiO was reduced to Ni-metal the rate of the reduction of nitric oxide was increased. It was furthermore shown that when Cu was present as CuO the reduction of oxygen was inhibited. But when CuO was reduced to $Cu_2O$ the reduction of oxygen was initiated.

Another possible class of oxide based electrodes is spinels. Several papers have been published using this class of oxides as cathodes for the electrochemical reduction of $NO_x$ [28–32]. In the first paper $CuCr_2O_4$ was investigated [28]. It was shown that $CuCr_2O_4$ only had a limited activity towards the reduction of nitric oxide. On the other hand $CuCr_2O_4$ showed some activity towards the oxidation of nitric oxide to nitrogen dioxide. In the next paper four spinels were characterized [29]. The four spinels had the following compositions: $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$ and $Co_3O_4$. The Ni and Cu containing spinels had a higher activity towards the electrochemical reduction of nitric oxide than towards the electrochemical reduction of oxygen. In contrast to this the cobalt containing spinels had either a higher or similar activity towards the electrochemical reduction of oxygen than towards the electrochemical reduction of nitric oxide. Later Bræstrup et al. measured on a series of spinels with the composition; $Ni_{1-x}Mg_xFe_2O_4$ where $x = 0.0, 0.3, 0.5, 0.6, 1.0$ [30]. The $MgFe_2O_4$ spinel had almost no activity towards the electrochemical reduction of oxygen, but had a high activity towards the electrochemical reduction of nitric oxide. It was also tried to replace part of the iron in $NiFe_2O_4$

with chromium, as the series $NiFe_{2-x}Cr_xO_4$ where 0.0, 0.5, 1.0, 1.5 and 2.0, was characterized [31]. It was shown that $NiCr_2O_4$ had a high activity towards the electrochemical reduction of nitric oxide compared to the activity towards the electrochemical reduction of oxygen. In the last study by Bræstrup et al. part of the iron in $MgFe_2O_4$ was replaced with manganese in an attempt to increase the electronic conductivity of the spinels [32]. However, replacement of iron with manganese leads to a decrease in the activity towards the electrochemical reduction of nitric oxide. In general it was shown that spinels with iron on the tetrahedral site had the highest activity towards the reduction of nitric oxide.

Kammer Hansen et al. also studied a large number of perovskite based cathodes for the electrochemical reduction of nitric oxide [28,33,34]. In the first paper the electrochemical reduction of nitric oxide and oxygen was studied on LSM15 and LSCo15 [33]. It was shown that both LSM15 and LSCo15 were active as electrodes for the electrochemical reduction of nitric oxide. The apparent selectivity, towards the electrochemical reduction of nitric oxide, of LSM15 was much larger than the apparent selectivity of LSCo15. In a later study a series of LSM perovskites was studied [28]. The intermediate perovskite LSM15 had the highest apparent selectivity towards the electrochemical reduction of nitric oxide. It was suggested that the redox capacity and the amount of oxide ion vacancies was determining for the rate of the reduction of nitric oxide. A series of iron-manganese based perovskites were also studied [34]. It was shown that the iron rich perovskites had the highest activity towards the electrochemical reduction of nitric oxide. The results confirmed the hypothesis that redox capacity and the amount of oxide ion vacancies is determining for the rate of the reduction of nitric oxide. The effect of adding BaO to the perovskites based electrodes was also investigated [35]. It was shown that the addition of BaO to the electrode leads to an increased apparent selectivity, but a lowered overall activity.

The group by Awano also studied perovskite based electrodes [40–42]. The activity of a LSM based cathode towards the reduction of nitric oxide was markedly increased when it was made as a composite with YSZ [40]. However, no information of the current efficiency was given. It was also shown that a composite cathode consisting of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ and CGO10 had the highest selectivity towards nitric oxide reduction when the electrode was made relatively thick [41]. Addition of Pt increased the selectivity towards nitric oxide reduction to 4% in the presence of 2% $O_2$ at 600 °C [42].

**Table 4**
Coating of noble metal based cathodes.

| Cathode, electrolyte | Temperature range | Concentration of NO | Concentration of $O_2$ | Selectivity | Current efficiency | Reference |
|---|---|---|---|---|---|---|
| $La_{1-x}Sr_xCoO_3$\|Pd, YSZ | 500 °C | 1000 ppm | 6% | – | – | [40] |
| $RuO_2$\|Ag, YSZ | 500 °C | 1000 ppm | 6% | – | 12% | [41] |
| YSZ\|NiO + YSZ\|Pt + YSZ, YSZ | 550–700 °C | 1000 ppm | 2% | – | 2.4% | [45–54] |
| $KNO_3$\|YSZ\|NiO + YSZ\|Pt + YSZ, YSZ | 200–400 °C | 1000 ppm | 1–10% | – | 10–20% | [58] |

Finally oxides with the $K_2NiF_4$ ($A_2BO_4$) structure were investigated by Simonsen et al. [36,37]. Using different ratios between lanthanum and strontium and either Ni or Cu as the B-site cation it was shown that $La_2CuO_4$ was the compound with the highest apparent selectivity. The activity of $A_2BO_4$ compounds is on the level with LSM.

*Coating of metal based electrodes.* The first example of coating of metal electrodes presented in the literature was in 1996 by Nakatani et al. [43]. Using palladium electrodes sintered at high temperature coated with $La_{1-x}Sr_xCoO_{3-\delta}$, they showed that this type of electrodes had a relatively high activity for the reduction of nitric oxide under oxidising conditions. The palladium electrode sintered at high temperatures was shown to form a dense layer on the surface of the electrolyte lowering the triple phase boundary area. The dense palladium electrode thereby inhibits the reduction of oxygen. However, the cells had a high internal resistance and the rate of the reduction of nitric oxide was when at its best only of the same order of magnitude as the rate of the reduction of oxygen (Table 4).

In a later study by the same group, different simple oxides were added to a dense silver electrode on a YSZ electrolyte [44]. Among the different oxides used silver electrodes coated with $RuO_2$ showed a high activity for nitric oxide reduction and a current efficiency up to approximately 12% was observed at a temperature of 500 °C. However, $RuO_2$ is highly carcinogenic and thereto comes that higher oxides of Ru is formed in an oxidising atmosphere. These higher oxides are volatile. $RuO_2$ is therefore not useful for practical applications.

In 2001 the group of Awano [45] suggested to use a multi-layered electrode structure with a Pt/YSZ cathode, a NiO/YSZ electro-catalytic active layer and a YSZ covering layer. Numerous studies of this type of electrodes have been published in the literature [45–54]. The effects of each of the three layers were studied in a series of papers [47,49,53]. It was shown that the activity of the cathode layer was much dependent on the Pt/YSZ ratio [47]. The highest current density was obtained with a volume fraction of YSZ slightly lower than 50%. The optimization of the electro-catalytic layer was also studied [49]. It was shown that a composite with 1/3 vol% of YSZ had the best properties for the activity of the cells towards the electrochemical reduction of NO. It was also shown that during operation some of the NiO is reduced to Ni-metal. The ability of Ni-metal to absorb and decompose nitric oxide molecules preferential to oxygen molecules is well known [55–57]. The effect of the YSZ covering layer is to suppress the adsorption and the decomposition of oxygen molecules [53]. Later an extra covering layer was added to the top of the multi-layered electrodes [58]. The layer was a $NO_x$ adsorbing layer consisting of Na, K or Cs together with platinum and alumina. The best results were shown using an adsorbing layer containing K. This type of electrode assembly leads to a current efficiency of up to 20%. The activity of this type of cathode was also quite high. It was calculated that an active electrode area of 0.9 m² at a temperature of 400 °C was needed in order to remove 500 ppm of nitric oxide in the exhaust gas of a 1.6 l diesel engine [10].

*Porous cell stacks.* A new electrochemical concept for removal of $NO_x$ was suggested by Werchmeister et al. [59]. Using a full ceramic porous cell stack, consisting of alternating layers of electrode and electrolyte, it was shown that nitric oxide could be reduced to nitrogen and oxygen, in the temperature range of 250–400 °C, when a potential was applied between top and bottom of the cell stack. The activity of the porous cell stack was markedly increased when the porous cell stack was impregnated with ceria or doped ceria. The activity of the porous cell stack towards the electrochemical reduction of nitric oxide was very low when oxygen was added to the gas feed stream. Therefore, this concept needs further development.

## 4. Conclusion

Good progress has been made in identifying electrodes for direct electrochemical reduction of nitric oxide under net oxidising conditions. It has been shown that several oxide based electrodes has a high apparent selectivity towards the reduction of nitric oxide. It has likewise been shown that coating of metal based electrodes can lead to current efficiencies of up to 20% even in the presence of high amounts of oxygen. Removal of nitric oxide using a full ceramic cell has been proved possible.

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